CURING CHARACTERISTICS AND PROPERTIES OF EPOXIDIZED NATURAL RUBBER (ENR)

BY

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DEDICATED

TO

MY GRAND PARENTS

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ABBREVIATIONS

ASTM	-	American Standards Test Methods
BR	-	Butadiene Rubber
BS	-	British Standards
CV	-	Conventional high-sulphur Vulcanization
CBS	-	N-Cyclohexylbenzothiazole-2-sulphenamide
CR	-	Chloroprene Rubber
DPG	-	Diphenylguanidine
DTDM	-	Dithiodimorpholine
DOTG	-	Di-o-tolylguanidine
EB	-	Elongation at break
ENR	-	Epoxidized Natural Rubber
EV	-	Efficient Vulcanization
EPDM	-	Ethylene-propylene-diene monomer
FTFT	-	Fatigue to failure test
II R	-	Butyl Rubber
IRHD	-	International Rubber Hardness Degree
MBT	-	2-Mercaptobenzothiazole
MPa	-	Mega-Pascal
MBTS	-	2-2'-Dithiobisbenzothiazole
NBR	-	Acrylonitrile Butadiene Rubber
NR	-	Natural Rubber

PVI	-	Prevulcanizing inhibitor
phr	-	Part per hundred of rubber
%	-	Percent
RHA	-	Rice husk ash
SBR	-	Styrene-butadiene Rubber
SMR	-	Standard Malaysian Rubber
semi-EV	-	semi-efficient vulcanization
TBBS	-	N-t-Butylbenzothiazole-2-sulphenamide
TMTM	-	Tetramethylthiuram monosulphide
TMTD	-	Tetramethylthiuram disulphide
Tg	-	Glass transition temperature
TETD	-	Tetraethylthiuram disulphide
ZDMC	-	Zinc dimethyldithiocarbamate
ZnO	-	Zinc oxide
kc	-	Kilocycles
t_5	-	Scorch time
Δt_L	-	Cure index
t_{90}	-	Cure time
θ	-	Rebound angle
E_a	-	Activation energy

ABSTRACT

The cure characteristics of accelerated sulphur vulcanization of epoxidized natural rubber containing 25 mol % of epoxidation (ENR 25) was studied while one grade of unmodified natural rubber - standard Malaysian rubber light (SMR L) was used as a control. The influences of different accelerator types - zinc dimethyldithiocarbamate (ZDMC), tetramethylthiuram disulphide (TMTD), diphenylguanidine (DPG), N-t-butylbenzothiazole-2-sulphenamide (TBBS), and 2-mercaptobenzothiazole (MBT) at various temperatures were investigated. Three vulcanization systems - conventional high-sulphur vulcanization (CV), semi-efficient vulcanization (semi-EV) and efficient vulcanization (EV) were also investigated. Mooney Shearing Disk Viscometer (MV 2000) and Moving Die Rheometer (MDR 2000) were used to determine the Mooney scorch time and cure time respectively in the temperature range of 100 to 180 ^{0}C. The results obtained indicate that Mooney scorch time and cure time decreases exponentially with increasing temperature for the two type of rubbers studied. At fixed curing temperature, ENR 25 shows shorter scorch time and cure time compared to that of SMR L. These differences in scorch behaviour and cure time is attributed to the activation of the double bond by the adjacent epoxide group in ENR 25. The investigation involving different accelerators show that mooney scorch time decreases in the order , TBBS > TMTD > DPG > MBT > ZDMC. Studies of the effect of varying amounts of MBT at a fixed sulphur concentration show

that scorch and cure time decrease as the accelerator concentration increases.

From this study it has been found that the cure index of SMR L is higher than that of ENR 25, especially at lower temperatures of study, i.e., 120 ^{0}C and below. This is attributed to the activation of double bonds by the adjacent epoxide group in the ENR compound. ENR 25 shows higher torque maximum than SMR L. This observation can be related to the oxirane group which is bulky and this accounts for increased glass transition temperature with increase in the level of epoxidation.

ENR 25 contains epoxide groups that activate the adjacent double bonds, thus a faster cure is observed. In all the vulcanization systems, CV shows the highest torque maximum followed by semi-EV and than EV. This differences are attributed to the amount of active sulphurating agent which increases with increasing accelerator concentration.

ENR 25 shows lower activation energy than SMR L for all the three different vulcanization systems and the accelerators studied. This is obviously due to the presence of epoxide groups that activate the adjacent double bonds, thus lowering the activation energy of vulcanization. However, some differences in the magnitude of cure time, cure index, torque maximum and activation energy in the temperature and accelerator studies are observed between ENR 25 and SMR L. It was also found that the influence of

accelerator/sulphur ratio becomes less significant as vulcanization temperature increases.

The physical and mechanical properties of SMR L and ENR 25 were also studied with three different fillers (i.e., carbon black, silica and calcium carbonate). The semi-efficient vulcanization system (semi-EV) was chosen rather than other vulcanization systems, because it is suitable for ENR. From this study, the physical and mechanical properties of carbon black, silica and calcium carbonate-filled ENR 25 shows higher modulus, hardness and fatigue life and less tensile strength, elongation at break, tear strength, resilience and abrasion loss than SMR L vulcanizates.

From scanning electron microscopy (SEM) of fracture surface of the samples subjected to fatigue to failure test (FTFT), the process of crack propagation is clearly demonstrated. It can be inferred from these micrographs that crack initiation and propagation can start from any part of the sample provided there is a flaw.

The ageing properties of filled ENR 25 and SMR L vulcanizates show similar trends. After ageing all the vulcanizates showed improvement in modulus, resilience, abrasion loss and hardness while tensile strength, elongation at break, tear strength and fatigue to failure decreased slightly. From this study, it can be said that overall ageing properties of ENR 25 shows similar trend as SMR L.

Tajuk : Ciri-Ciri Pematangan dan Sifat-Sifat untuk Getah Asli Terepoksida (ENR)

ABSTRAK

Sifat-sifat pematangan bagi pemvulkanan getah asli terpoksida yang mengandungi 25 % mol pengepoksidaan (ENR 25) terpecut sulfur telah dikaji sementara getah asli (SMR L) telah digunakan sebagai kawalan. Kesan berbagai pemecut - zink dimetilditiokarbamat (ZDMC), tetrametiltiuram disulfida (TMTD), difenilguanidin (DPG), N-t-butilbenzotiazol-2-sulfenamida (TBBS) dan 2-merkaptobenzotiazol (MBT) pada suhu yang berlainan dikaji. Tiga jenis sistem pemvulkanan - pemvulkanan konvensional bersulfur tinggi (CV), pemvulkanan semi-efektif (semi-EV) dan pemvulkanan efektif (EV) juga telah dikaji. Mooney Shearing Disk Rheometer (MV 2000) dan Moving Die Rheometer (MDR 2000) masing-masing telah digunakan untuk menentukan masa skorj Mooney dan masa pematangan di dalam julat suhu 100°C hingga 180°C. Keputusan yang didapati menunjukkan bahawa masa skorj Mooney dan masa pematangan berkurang secara eksponen dengan peningkatan suhu bagi kedua-dua jenis getah tersebut. Pada suhu pematangan yang ditetapkan, ENR 25 menunjukkan masa skorj dan masa pematangan yang lebih pendek

berbanding dengan SMR L. Perbezaan dalam kelakuan skorj dan masa pematangan ini wujud disebabkan oleh pengaktifan ikatan dubel oleh kumpulan epoksi yang berada bersebelahan dengan ikatan dubel tersebut di dalam ENR 25. Kajian ke atas berbagai pemecut menunjukkan bahawa masa skorj Mooney berkurang mengikut turutan berikut: TBBS > TMTD > DPG > MBT > ZDMC. Kajian ke atas pelbagai amaun MBT pada satu nilai kepekatan sulfur yang tetap menunjukkan bahawa masa skorj dan masa pematangan berkurang apabila nilai kepekatan pemecut meningkat.

Daripada kajian ini, didapati bahawa indeks pematangan bagi SMR L adalah lebih tinggi daripada ENR 25, terutamanya pada suhu yang lebih rendah, iaitu 120°C dan ke bawah. Ini adalah disebabkan oleh pengaktifan ikatan dubel oleh kumpulan epoksi yang berada bersebelahan dengan ikatan dubel tersebut di dalam sebatian ENR 25. ENR 25 menunjukkan nilai tork maksimum yang lebih tinggi daripada SMR L. Ini adalah kerana kumpulan oksirana merupakan suatu kumpulan yang besar, maka suhu peralihan kaca akan meningkat dengan meningkatnya darjah pengepoksidaan. ENR 25 mengandungi kumpulan epoksida yang boleh mengaktifkan ikatan dubel yang bersebelahan dengannya, maka suatu pematangan yang cepat dapat diperhatikan. Di antara semua sistem pemvulkanan, CV menunjukkan tork maksimum yang paling tinggi, diikuti oleh semi-EV dan EV. Perbezaan ini bergantung kepada jumlah agen sulfur yang aktif yang mana ianya akan meningkat dengan meningkatnya kepekatan pemecut.

ENR 25 memberikan tenaga pengaktifan yang lebih rendah berbanding dengan SMR L bagi ketiga-tiga sistem pemvulkanan dan ke semua pemecut yang dikaji. Ini adalah jelas disebabkan oleh kehadiran kumpulan epoksi yang bertindak mengaktifkan ikatan dubel yang terdapat bersebelahan dengannya, yang mana akan mengurangkan tenaga pengaktifan bagi pemvulkanan tersebut. Walau bagaimanapun, beberapa perbezaan di antara ENR 25 dan SMR L dapat diperhatikan di dalam magnitud masa pematangan, indeks pematangan, tork maksimum dan tenaga pengaktifan bagi kajian ke atas suhu dan pemecut. Kesan nisbah pemecut/sulfur juga diperhatikan menjadi kurang berkesan apabila suhu pemvulkanan ditingkatkan.

Sifat-sifat fizikal dan mekanikal bagi SMR L dan ENR 25 dengan penambahan tiga jenis pengisi yang berlainan (hitam karbon, silika dan kalsium karbonat) juga dikaji. Sistem pemvulkanan semi efektif (semi-EV) telah dipilih di antara sistem-sistem yang lain kerana ianya sesuai untuk ENR. Daripada kajian ini, didapati bahawa sifat-sifat fizikal dan mekanikal bagi ENR 25 terisi hitam karbon, silika dan kalsium karbonat telah menunjukkan modulus, kekerasan dan hayat fatig yang lebih tinggi dan kekuatan tensil, pemanjangan pada takat putus, kekuatan cabikan, resiliens dan kehilangan pelelasan yang lebih rendah berbanding dengan vulkanisat SMR L.

Daripada kajian Mikroskop Pengskanan Elektron (SEM) ke atas permukaan putus sampel selepas ujian kegagalan fatig dilakukan (FTFT), didapati bahawa perembatan retak dapat diperhatikan dengan jelas. Daripada mikrograf-mikrograf ini, dapatlah dikatakan bahawa permulaan dan perambatan retak boleh bermula daripada sebarang bahagian daripada sampel tersebut.

Sifat-sifat penuaan bagi ENR 25 dan SMR L telah menunjukkan pola yang sama. Selepas penuaan, semua sebatian menunjukkan peningkatan dalam modulus, resiliens, kehilangan pelelasan dan kekerasan manakala kekuatan tensil, pemanjangan pada takat putus, kekuatan cabikan dan kegagalan fatig pula didapati berkurang. Daripada kajian ini, dapatlah dikatakan bahawa secara keseluruhannya sifat-sifat penuaan ENR 25 menunjukkan pola yang sama seperti SMR L.

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

Elastomers are sometimes randomly referred to as rubbers. More appropriately, a rubber may be a natural material or synthetic polymer. Such a large number of rubber-like polymers exist, that the broad term elastomer is most fitting and most commonly used to describe them.

Natural rubber (NR) is generated in the *Hevea brasiliensis* tree as an emulsion of cis-polyisoprene and water, known as latex during the 1920s. The latex is coagulated and then dried to produce a clear crepe rubber. Natural rubber was the only rubber available for more than a century but the growth in the demand for tyres has out-stripped the available supply and today NR represents less than 33% of the total usage of rubber. World consumption of NR is in excess of 4 million tonnes per year with Malaysia as the 3rd largest single producer.

Since World War II, most of the widely used types of synthetic rubber have become available in latex form. Styrene-butadiene (SBR) copolymer latices, with styrene contents in the range 25 - 50 % and total solids contents of 40 - 65 %, are supplied by a number of producers. Chloroprene (CR) and nitrile (NBR) rubber latices are available with solids content up to 50 %. These have supplemented and replaced the natural product for a number of

applications. The CR and NBR have oil and solvent resistance, which is taken advantage of in gloves and bonded fabrics designed to withstand dry-cleaning. The fire -retardant property of CR is also exploited.

Epoxidized natural rubber (ENR) is a chemically modified natural rubber (NR) [1 - 5] which in addition to retaining some of the advantages of NR exhibits characteristics similar to some synthetics [4,5]. Natural rubber is very versatile and the vulcanization type is determined by the intended use. But it was soon realized that this is not the case with ENR. ENR cured with the conventional vulcanization system (CV) was found to exhibit poor ageing properties [4 - 6]. In CV systems the ratio of sulphur is higher than the accelerator leading to the formation of crosslinks which are predominantly polysulphidic. Although CV cured vulcanizates show good fatigue properties, their ageing characteristics are not as good as efficient vulcanization (EV) cured vulcanizates. Consequently, the use of semi-efficient (semi - EV) vulcanization system in which the sulphur to accelerator ratio are about the same was found to be more suitable [4 - 6]. Semi-EV cured compounds exhibit properties which are intermediate between CV and EV. Efficient vulcanization yields mainly monosulphidic crosslinks as the ratio of accelerator is higher than that of sulphur. This reflects the importance of sulphur to accelerator ratio in ENR compounding which in effect determines the nature of sulphur crosslinks. The recommendations favouring semi - EV were based mainly on vulcanizate properties while the vulcanization characteristics are still largely unexplored. Some studies have been reported on conventional vulcanization systems [7-9]. Most of the studies on ENR

concentrated on its physical and mechanical properties [2,5,10 - 16] or miscibility with other polymers [17 - 23] and fewer studies on the cure characteristics have been reported [2,8,9,24,25].

While the few studies conducted on the cure characteristics of ENR are mainly on scorch and reversion [2,8,9,24,25] , studies on cure kinetics (activation energy), cure rate and different vulcanization systems are rather limited. In view of the importance of curing characteristics, it is the aim of this study to describe further some of the findings in this area of research.

As this project deals mainly with cure kinetics, cure rate, optimum cure, and properties, the main cure characteristics and properties of rubber compounds are briefly discussed next.

1. 1. 1 CURE CHARACTERISTICS

Curing or vulcanizing is a process whereby a rubber compound is converted to a strong elastic material. Curing process can be described by a Rheometer curve (Fig. 1.1). The curve has three stages : (i) Induction and Scorch, (ii) Curing and (iii) Over cure [26]. The period of time before vulcanization starts is referred to as 'scorch time' or scorch delay. Scorch is premature vulcaniation in which the rubber compound becomes partly vulcanized before the product is in its final form and ready for vulcanization. It reduces the plastic properties of the compound so that it can no longer be processed.

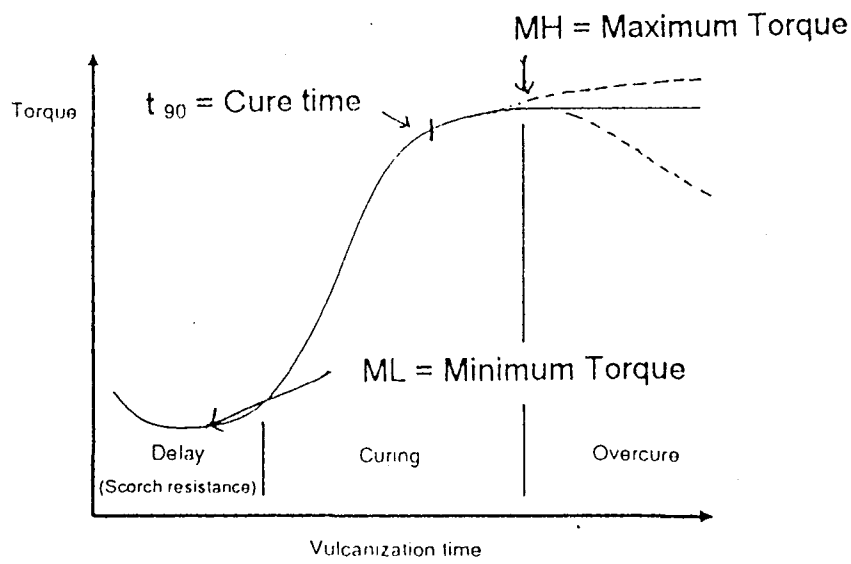


Figure 1. 1 Steps in the vulcanization process [75].

Scorching is the result of both the temperature reached during processing and the amount of time the compound is exposed to elevated temperature.

The rate of cure is the rate at which crosslinking and the development of the stiffness (modulus) of the compound occur after the scorch point. As the compound is heated past the scorch point, the properties of the compound change from a soft plastic to a tough elastic material required for use. During the curing step crosslinks are introduced, which connect the long polymer chains of the rubber together. As more crosslinks are introduced, the polymer chains become more firmly connected and the stiffness or modulus of the compound increases. The rate of cure is an important vulcanization

parameter which determines the time the compound must be cured, i. e., the cure time. 'Cure time' is the time required during the vulcanization step for the compounded rubber to reach the desired state of cure.

' Overcure ' is a cure which is longer than optimum. The state of cure is a term used to indicate the development of a property of the rubber as cure progresses. As the crosslinking or vulcanization proceeds, the modulus of the compound increases to various state of cure . Overcure may be of three types. In one type known as marching cure, the rubber continues to harden, the modulus rises, and tensile strength and elongation fall. In another type, reversion of overcure, the modulus and tensile strength decreases. The third is plateau cure in which, the properties remain constant.

Studies on the cure characteristics of natural rubber (NR) are well documented [27 - 50] whereas those based on epoxidized natural rubber (ENR) are rather limited [2,8 - 12, 24,25]. Earlier workers [27 - 29] had determined that sulphenamide accelerators reacted with sulphur to form various polythiobenzothiazole intermediates during the cure delay period of vulcanization, and that these species reached a maximum concentration just prior to crosslinking. Coincident with the onset of crosslinking is the depletion of the original accelerator. Campbell and Wise [27,28] proposed that the cure delay period is due to the preferential reaction of the polythiobenzothiazole with the original accelerator rather than with the rubber to form crosslinks. Coran [29,30] in his kinetic model based on the same analytical results, suggests that the accelerator and / or its immediate reaction

products with sulphur act to inhibit the formation of crosslinks. This inhibition was thought to result from a quenching of an activated form of the polymeric polysulphide, which would otherwise go on to form crosslinks. In any event, the length of the delay period should largely depend on the time required for the disappearance of the accelerator. Duchacek [31] suggested the probability that the inhibition effect of 2 - mercaptobenzothiazole (MBT) is attributable to the formation of a complex with zinc dimethyldithiocarbamate (ZDMC) which decreases the reaction rate in the initial steps of the sulphur - free thiuram vulcanization and thus causes scorch delay.

The vulcanization process produces several types of crosslink structures including mono-, di-, and polysulphidic linkages [32 - 34]. It is well established that the structure varies with the time and temperature of vulcanization. It is anticipated that a knowledge of the mechanism of accelerated sulphur curing could lead to a prediction of the type of crosslinks which will predominate under different vulcanization conditions. The rate and state of cure have been reported by Juve [35]. Thompson and Watts [36] showed that cure time depends on the shape and size of molding, the molding temperature and the accelerator system. Loo [37] showed that decrease in crosslink density at high curing temperature was mostly due to decrease in polysulphidic crosslinks. The formation of intramolecular sulphidic group and zinc sulphide increases with temperature. A dynamic shear modulus was measured during the progress of vulcanization and reversion thus obtaining a complete curve of modulus vs. cure time on a single specimen by Peter and Heidmann [38] and by Payre [39]. Davies [40]

discussed the influence of cure time and temperature on the density and distribution of crosslinks in natural rubber vulcanizates. Generally, during vulcanization the crosslinks formed initially are mainly unstable polysulphidic ones. These are transformed to di-, and monosulphidic crosslinks as cure progresses through optimum and into overcure. Reversion occurs when continued curing causes the polymers to exhibit a loss of physical and mechanical properties such as tensile strength, stiffness, resilience, and wear resistance. Generally, it is accepted that reversion occurs because desulphuration takes place too slowly during vulcanization [41- 43]. Reversion may also be caused by thermal depolymerization of the polymer chain [44]. Efficient vulcanization systems have been found to have better reversion resistance than conventional curing system [45]. Much work has been done on the reversion process, most of which has been concerned with the changes in the chemical structure of vulcanization [46,47]. Chen et al. [47,48] examined the effect of some compounding variables on the reversion process but they need exceptionally large dosages of sulphur , which in practice are quite different from those normally used in the conventional systems for NR. Bristow [49] examined the effect of zinc soap and stearic acids on the reversion of thiazole and sulphenamide accelerated vulcanization of natural rubber. Kok [50] showed that fast accelerators give higher reversion compared to that of slower accelerators. His work suggests that reversion appears to be typical only for the polyisoprene structure.

1. 1. 2. VULCANIZATE PROPERTIES

The effect of vulcanization system on the properties of natural rubber are well-established, but comparatively little data have been presented on ENR. The epoxidation of natural rubber and other unsaturated polymers has been reported [51 - 57]. However, there is little data available on the properties of the products and in some cases the results are conflicting. It has been claimed that epoxidation of unsaturated polymers increases wear and improves solvent resistance, tensile strength and other mechanical properties [57], whereas other workers have reported a reduction in strength properties [58,59]. Baker et al. [60] found that compounding with CV systems as normally used with NR are not suitable for ENR. The reason for this is the reaction of the epoxide groups with the sulphur acids produced by the ageing of the polysulphide crosslinks. This ring opens the epoxide groups, leading to crosslink formation and subsequent increase in hardness and modulus. This in turn reduces properties such as tensile strength, tear strength and fatigue. Silica's and silicates of varying forms and particle sizes have been widely used as reinforcing fillers in rubbers. Their properties are usually inferior to those of carbon blacks. The high viscosity of a silica-filled rubber makes it more difficult to process [61,62]. Mechanical and dynamic properties of silica-filled vulcanizates, with the addition of silane based coupling agents is well known and has been studied by many workers such as Wagner [54,63], Dannenberg [64], Cameron et al. [65] Fetterman [66], and Nasir et al. [13,67].

Baker et al. [2] reported that, in the CV system, ENR shows poorer performance characteristics, when compared with unmodified NR. Whereas, Gelling [10] reported that ENR shows better performance with a semi-EV system. Nasir et al. [13] found that semi-EV system was better than either CV or EV systems when ENR is mixed with silica, with or without the addition of a silane coupling agent. High tensile properties comparable to N330 carbon black reinforcement could be obtained [13]. Unlike NR, ENR has the ability to be reinforced with silica without silane coupling agent [68]. The addition of a silane coupling agent into silica-filled ENR would further enhance the physical properties. Chemical crosslinking or chemical interaction between the epoxy groups and silanol groups has been cited to be the reason for the unusual reinforcement [69]. Recently studies on (RHA) rice husk ashes-filled ENR vulcanizates have been reported by some workers such as Fuad et al. [70,71], Ishak et al. [72,73] and Hanafi et.al. [74]. Hanafi et al. also found that semi-EV system was better than CV or EV systems when ENR is reinforced with RHA, with or without the addition of silane coupling agent.

While the few studies conducted so far on the cure characteristics of accelerated - sulphur vulcanization of ENR are limited to scorch and reversion behaviour [2,8,9,24,25], studies on the cure kinetics and characteristics are yet to be reported in literature. Cure characteristics depends on the type of elastomers, accelerator system, temperature, cure kinetics, cure rate and also filler types. In view of the importance of curing characteristics and its effect on the properties of epoxidized natural rubber

vulcanizates, it is the aim of this study to describe further some of the findings in this area of research.

1. 2. LITERATURE REVIEW

1. 2. 1. HISTORY OF SULPHUR VULCANIZATION

INTRODUCTION

Tires and mechanical goods which are very useful rubber articles cannot be made without vulcanization. Unvulcanized rubber is generally not very strong, does not maintain its shape after a large deformation and can be very sticky. Charles Goodyear has been accredited with the first commercially recognized method of vulcanization [75]. In 1841 his process of heating natural rubber with sulphur was first successfully used. In addition to natural rubber, many synthetic rubbers have been introduced. Also, in addition to sulphur, many other substances have been introduced as components of curing (vulcanization) systems. Emphasis is placed on the vulcanization of general purpose "high-diene" rubbers (e.g., natural rubber (NR), styrene-butadiene rubber (SBR) and butadiene rubber (BR)) by sulphur in the presence of organic accelerators. The accelerated-sulphur vulcanization of these rubbers along with the vulcanization of other rubbers which are vulcanized by closely related technology (e.g., ethylene-propylene-diene monomer rubber (EPDM), butyl rubber (II R), halobutyl rubber and nitrile rubber (NBR) comprise more than 90% of all vulcanization [75].

DEFINITION OF VULCANIZATION

Vulcanization is a chemical process by which plastic rubber is converted into the elastic rubber or hard rubber state. During vulcanization:

(I). the long chains of polymer molecules become crosslinked by reactions with the vulcanization agents to form three dimensional structures. This transforms the soft plastic-like material into a strong elastic product.

(II). the rubber looses its tackiness and becomes insoluble in solvents and it is more resistant to deterioration caused by heat, light and ageing process [76].

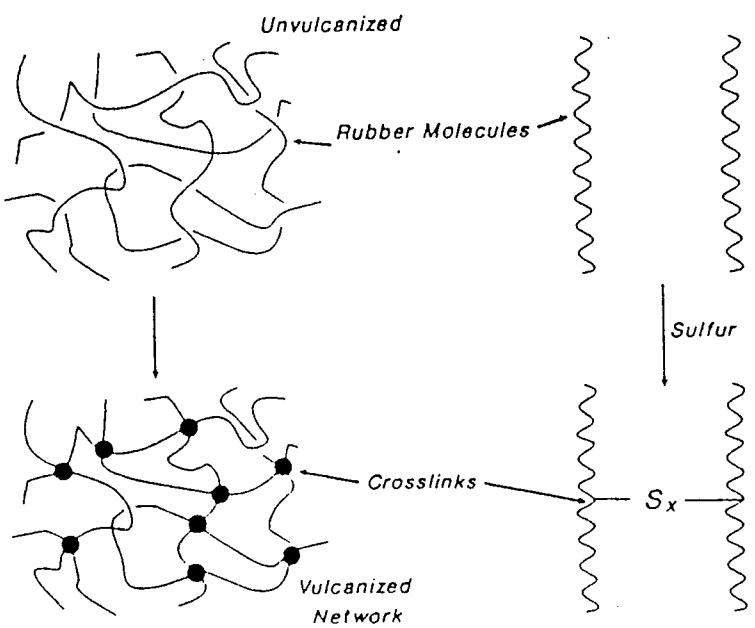
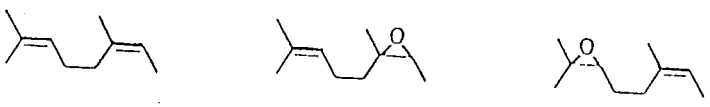


Figure 1. 2 : Crosslinked molecular network formation [75].

The vulcanization of ENR by sulphur alone is significantly faster than that of NR and a much higher degree of crosslinking is achieved. Experiments with model compounds [11] have shown that the olefinic groups and not the epoxides are the site of crosslinking and that the presence of epoxide groups has little effect on the distribution of mono- and di-sulphides. Sulphur reacts with olefins by a chain mechanism and the slower rate of reaction of compounds such as **A** has been stated [77] to be due to cyclization of a chain propagating species. In randomly epoxidized ENR-50 the majority of olefin groups are adjacent to an epoxide and thus the cyclization is blocked. This may not be the only cause as compounds **B** and **C** exhibited a greater extent of reaction than a mixture of **D** and **E**, indicating an additional activation when epoxide and olefin moieties are in the same molecule.



A **B** **C**

D **E**

In the presence of sulphenamide accelerators the model olefin **D**, alone and in the presence of epoxide **E**, yields qualitatively similar sulphides, but the epoxide affected the relative amounts of the sulphides [11].

1. 2. 2. COMPONENTS OF A RUBBER COMPOUND

Compounding ingredients can be classified into ten major categories.

a. Elastomers (rubbers)

b. Vulcanizing agents

c. Accelerators

d. Activators and retarders

e. Antidegradants (antioxidants, antiozonats, protective waxes)

f. Processing aids (peptizers, lubricants, release agents)

g. Fillers (carbon blacks, non-black materials)

h. Plasticizers, softeners, and tackifiers

i. Colour pigments

j. Special purpose materials (blowing agents, deodorants, etc.)

1. 2. 2. a. ELASTOMERS (RUBBERS)

The most important and the first step in compounding is the selection of a base elastomer or elastomers. The common basic characteristics of all elastomers are, their elasticity, flexibility, toughness, and relative impermeability to both water and air. Beyond these common characteristics, each elastomer has its own unique properties [78].

1. 2. 2. b. VULCANIZING AGENTS

Vulcanizing agents are the second most important chemicals in compounding. They are used to cause chemical reactions, resulting in crosslinking of elastomer molecules which transforms a soft, tacky

thermoplastic to a strong temperature-stable thermoset. Sulphur is by far the most widely used vulcanizing agent. Sulphur-bearing materials such as thiuram disulphides (TMTD) and dithiodimorpholine (DTDM) are sometimes used as complete or partial replacements of elemental sulphur in a low sulphur or sulphur-less cure system to improve the heat resistance of a compound [78].

1. 2. 2. c. ACCELERATORS

Accelerators are the second most important chemicals in compounding. They are used to reduce the vulcanization time, or cure time, by increasing the speed of vulcanization. Most accelerators in used today are organic substances containing both nitrogen and sulphur. The thiazoles are by far the most widely used accelerators [79]. Accelerator has a profound influence on the nature of crosslinking, which largely determines the physical properties (tensile strength, modulus, resilience, etc.) the resistance to ageing, and the processing characteristics (scorchiness and cure rate) [78].

1. 2. 2. d. ACTIVATORS AND RETARDERS

Activators are used to activate the accelerator and improve its effectiveness. The most widely used activators are zinc oxide (ZnO), and stearic acid (or fatty acid). A cure system consisting of sulphur and organic accelerators usually requires the presence of adequate zinc oxide and stearic acid to attain good crosslinking efficiency [80].

The retarders are used to reduce the scorchiness of a compound. The most widely used true retarder is cyclohexyl-N-thiophthalimide. It makes a sulphenamide or thiazole accelerated compound much less scorchy and gives it more processing safety without affecting its cure rate or vulcanization properties. Sodium acetate, phthalic anhydride, and salicylic acid, are not true retarders because they reduce both scorchiness and cure rate [78].

1. 2. 2. e. ANTIDEGRADANTS

Antidegradants are used to retard the deterioration of rubber compounds initiated by oxygen, ozone, heat, light, metal catalysis, and mechanical flexing. An antidegradant is needed to impart good ageing properties to a compound and extend its useful life. Its relative effectiveness is in various areas of protection. Waxes are often used with antidegradants to provide a protective coating which shields the rubber vulcanizate from the effect of ozone [78].

1. 2. 2. f. PROCESSING AIDS

Processing aids are used to facilitate processing operations, such as mixing, calendering, extrusion, and moulding. These include peptising agents, softeners (oil and waxes) and plasticizers. Peptizers help greatly in the breakdown of natural rubber during mastication [76,81]. They act as catalysts for oxidative breakdown during milling and internal mixer mastication. SBR, CR or EPDM do not generally require peptizers [82].

1. 2. 2. g. FILLERS

Fillers are the third most important materials in compounding. These are used to reinforce physical properties, to impart certain processing characteristics or to reduce cost. A reinforcing filler enhances hardness, tensile strength, modulus, tear strength and abrasion resistance of a compound. It is usually either a carbon black or a fine-particle mineral pigment [78]. A reinforcing filler has a profound influence on a processing characteristics and vulcanizate properties. The properties and processibility of a carbon black reinforced compound is greatly affected by the particle size and structure of the type of black [83]. The degree of reinforcement increases with a decrease in particle size. The finer fillers require more energy for their dispersion into the elastomer and are therefore more difficult to process. The particle size of a filler plays a major role in the tensile strength of rubber vulcanizates. Vulcanizates containing small particle size blacks produce the high tensile strength at optimum loading. Carbon blacks activate cure [84].

Mooney viscosity is dependent on carbon black structure and loading. High structure blacks contribute the highest Mooney viscosity with particle size having a lesser effect. Mooney viscosity rises rapidly with increase in loading except for thermal blacks where loading does not seem to have much effect [78]. Mooney scorch also varies with particle size. The largest particle blacks give the greatest scorch resistance, while high structure , small particle-size blacks usually reduce scorch resistance.

Non-black reinforcement is obtained through the use of pure silica type materials which are capable of very good physical properties. These are specially used with synthetic rubbers [85]. Extending with non-black materials such as china clay, talc and / or whiting help to keep the cost down as well as "smooth" out the compound to help its processability, especially in extending calendering operations. The choice of fillers should also be based on suitability in the service environment of the product e.g. if acid resistance is required, whiting calcium carbonate is unsuitable [83].

The effect of a particulate filler on a rubber depends on the following factors :

1. The surface area of the filler particles. This is directly related to the particle size; the lower the particle size, the higher the surface area.
2. The chemical nature of the particle surface. It can vary among different fillers.
3. Geometrical characteristics. Under an electron microscope, the primary particles of carbon black are fused into larger aggregates. The size, shape and number of voids in this ' aggregate ' determine the ' structure ' of the carbon black, and this structure can influence the physical and processing properties obtained.

Porosity of the filler particle is a factor that influences the properties obtained. Silicas are generally more porous than carbon black, and thus silica fillers give higher viscosity compounds at equal volume loading.

1. 2. 2. h. PLASTICIZERS, SOFTENERS AND TACKIFIERS

Plasticizers, softeners and tackifiers are used to either aid mixing, modify viscosity, produce tack, provide flexibility at low temperatures, or replace a portion of the base polymer without substantial loss in physical properties [76]. The important criteria of plasticizers are elastomer compatibility, efficiency, stain resistance, and cost. Insoluble plasticizers will bleed out and cause poor physical properties and surface stickiness. Aromatic type oil is not compatible with natural rubber, Isoprene, Butyl rubber and EPDM. Paraffinic type oil is not compatible with SBR, Butadiene, Nitrile, and Neoprene rubbers [82].

The most effective plasticizers are also good solvents for the elastomers, they impart softness to the compound but do not reduce its "nerve". They also give good resilience and reduce the hardness of the vulcanizates. Low boiling plasticizers would lose their effectiveness during processing and thus lose their effectiveness. The viscosity of the plasticizer influences the hardness of the vulcanizates [78].

1. 2. 2. i. COLOUR PIGMENTS

Colour pigments are used to impart specific colouring to a non-black rubber compound. Colour pigments are divided into two groups, inorganic and organic [83]. Most widely used inorganic pigments are oxides of iron, chromium, and titanium and the sulphides of cadmium, antimony, and mercuric, nickel titanate, and ultramarine blue. Organic dyes are much more expensive than inorganic pigments. Their advantages are high efficiency,

brilliancy in colour and much lower specific gravity. Organic dyes can provide many delicate shades which are not possible to obtain with inorganic pigments. Most organic dyes are not stable to steam, light, and acid or alkali solution. Some of them have a tendency to migrate to the surface. A combination of inorganic and organic pigments usually produce a better overall result in terms of brilliancy and stability [78].

1. 2. 2. j. SPECIAL PURPOSE MATERIALS

Special purpose materials are used for specific purposes which are not normally required in the majority of rubber compounds. Blowing agents, deodorants, adhesion promoters, flame retardants, fungicide, and UV light absorbers are some of the ingredients which can be added as required [78].

Since this research is focused on the type of rubber i.e. ENR , sulphur/accelerator ratio, and the effect of various accelerators among others, these are discussed in detail, further in the text.

1. 2. 3. Epoxidized Natural Rubber (ENR)

Epoxidized natural rubber (ENR) is a chemically modified form of natural rubber (cis-1,4-polyisoprene) in which some of the unsaturation is converted into epoxide groups which are randomly distributed along the polymer chain. The epoxidization of natural rubber has been investigated since the 1922's [86]. Earlier natural rubber latex was reacted with peracids to produce

epoxidized natural rubber (Fig. 1. 3), which contains secondary ring-opened products that were neither useful nor reproducible [4,10,11].

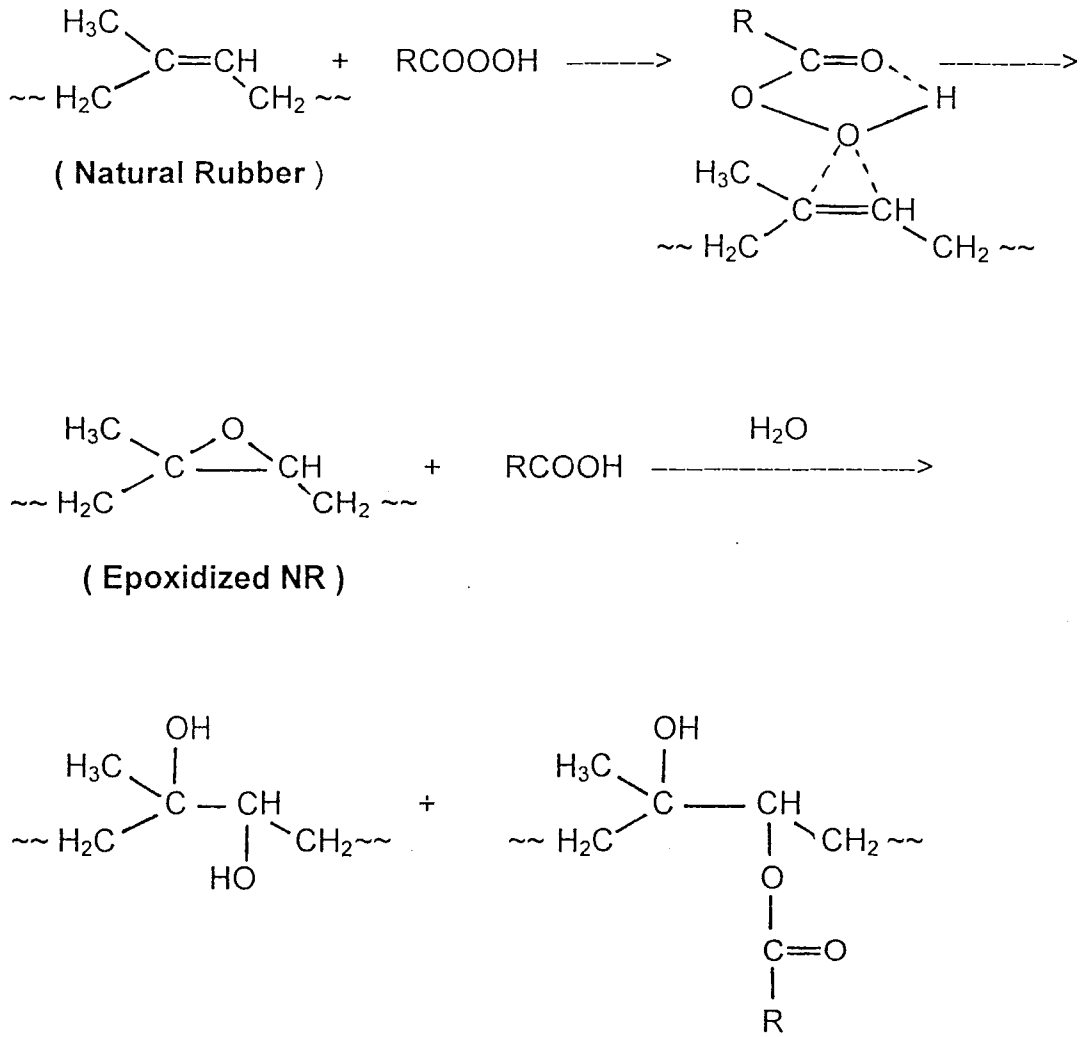


Figure 1. 3 Mechanism of epoxidation of NR with a peracid and subsequent secondary ring-opening reaction [87].

But the commercial viability and the potential application of epoxidized NR were fully realised only in the last decade or so. Gelling [87] showed that any desired degree of clean epoxidation was possible under controlled conditions. Under controlled conditions, epoxidized NR (Fig. 1. 4) were prepared from

Malaysian LA -TZ latex concentrate either by reaction with peroxyethanoic acid solution [10] or by generating peroxymethanoic acid in *situ* from hydrogen peroxide and formic acid [87].

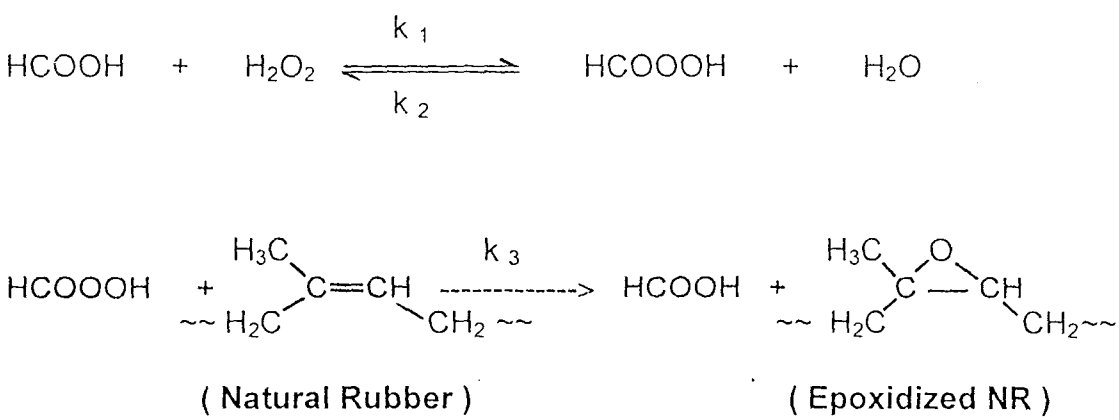


Figure 1. 4 In *situ* epoxidation of natural rubber employing hydrogen peroxide and methanoic acid [87].

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy shows that these materials are free from any other chemical modification. The later technique was also employed [10] to study the distribution of epoxide groups along the NR back bone. Up to 90 mole % epoxidation is possible by changing parameters such as dry rubber content of the latex, hydrogen peroxide/acid ratio, reaction temperature and duration.

Epoxidation is a stereospecific and random reaction, which retains some of the typical properties of natural rubber. Controlled epoxidation of NR gives a systematic increase in the polarity and glass transition temperature (Tg) of ENR produced [4,10,87]. As a result ENR has increased resistance to

hydrocarbon oils and higher hysterises, low air permeability, increased damping and better bonding to polar elastomers, and retains a great deal of the strain crystallization of natural rubber and hence has superior tensile and fatigue properties [14].

ENR can be crosslinked by any system used to cure unsaturated polymers but a sulphur based semi-efficient vulcanization (Semi-EV) or efficient vulcanization (EV) type formulation is preferred [2,4,88]. Conventional high-sulphur vulcanization (CV) systems are not recommended for ENR because of their poor ageing characteristics [11]. ENR has high degree of reinforcement with silica fillers in the absence of coupling agents [2]. High tensile properties comparable to carbon black reinforcement could be obtained [13]. ENR is an elastic and polar material. So it is quite unique and a versatile material suitable for various applications especially in the realm of thermoplastic elastomers [5,13].

Many studies on the physical and mechanical properties of ENR have been reported [2,5,8,10,13 -15]. Epoxidation is a stereospecific reaction, i.e., cis-olefin undergoes cis-epoxidation [87]. An x-ray study [14] of ENR gum vulcanizates has confirmed that ENR undergoes strain-induced crystallization. Ageing behaviour [11,12,16], and blending [17 - 19], of epoxidized natural rubber were also reported. Investigation of other properties for the purpose of application favours 50 mole % of epoxidation of natural rubber [2,4,10,11,87]. Recently studies on the scorch [9] and reversion [25] behaviour of epoxidized NR have been reported.

1. 2. 4. TYPES OF ACCELERATORS AND THEIR APPLICATIONS

Accelerators can be classified by their chemical type.

a. Guanidine's.

b. Dithiocarbamates.

c. Thiuramsulphides.

d. Thiazoles.

e. Sulphenamides.

1. 2. 4. a. GUANIDINES

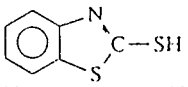
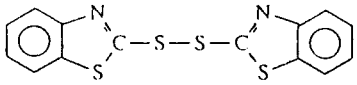
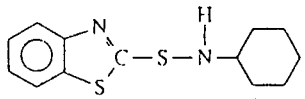
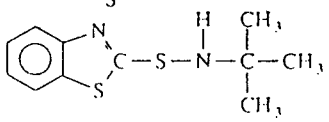
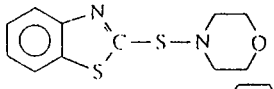
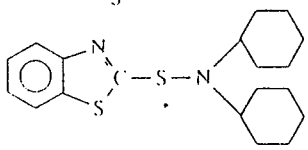
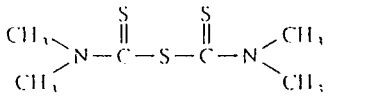
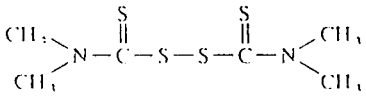
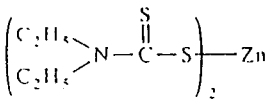
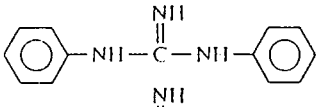
The guanidines are used as primary accelerators because of their slow curing. Diphenylguanidine (DPG) and diorthotolylguanidine (DOTG) are the two main guanidine accelerators [79]. Their main use is being a secondary accelerator in thiazole- or sulphenamide-accelerated natural rubber or SBR stocks. Both are white powders, guanidines can stain to some extent so they are not used in the best white or light-coloured stocks [89].

1. 2. 4. b. DITHIOCARBAMATES

Dithiocarbamates are made from the metal and amine salts of dithiocarbamic acids. They are called ultra-accelerators because of their quick curing characteristics. Very common members of this class are the zinc methyl and ethyl dithiocarbamates [79]. Dithiocarbamates are so powerful that they are used alone, and cured in air at room temperature or slightly elevated temperatures [90]. Usually they are paired with thiazole or sulphenamide accelerators to adjust the cure rate of a stock. Usually nonstaining, the

thiocarbamates are versatile accelerators and are used in butyl rubber (IIR) and ethylene-propylene-diene monomer (EPDM) as well as NR and SBR.

Table 1.1 : Accelerators for Sulphur Vulcanization [75].

Compound	Abbreviation	Structure
Benzothiazoles		
2-Mercaptobenzothiazole	MBT	
2-2'-Dithiobisbenzothiazole	MBTS	
Benzothiazolesulfenamides		
N-Cyclohexylbenzothiazole-2-sulfenamide	CBS	
N-t-Butylbenzothiazole-2-sulfenamide	TBBS	
2-Morpholinothiobenzothiazole	MBS	
N-Dicyclohexylbenzothiazole-2-sulfenamide	DCBS	
Dithiocarbamates		
Tetramethylthiuram monosulfide	TMTM	
Tetramethylthiuram disulfide	TMTD	
Zinc diethyldithiocarbamate	ZDEC	
Amines		
Diphenylguanidine	DPG	
Di-*o*-tolylguanidine	DOTG